

1260515

NO DRAWINGS

(21) Application No. 15938/69 (22) Filed 26 March 1969
 (31) Convention Application No. 724 602 (32) Filed 26 April 1968 in
 (33) United States of America (US)
 (45) Complete Specification published 19 Jan. 1972
 (51) International Classification C 11 d 1/00, 1/02, 3/16
 (52) Index at acceptance
 C5D 6A5D2 6A5E 6B11A 6B12B1 6B12F1 6B12F2
 6B12G2A 6B12G2B 6B12G2C 6B12L 6B13 6B7
 6C8



(54) ANTIREDÉPOSITION AGENT FOR USE IN
 SYNTHETIC DETERGENTS

(71) We, BORG-WARNER CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 200 South Michigan Avenue, 5 Chicago, Illinois 60604, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and 10 by the following statement:—

This invention relates to detergent compositions having improved antiredéposition characteristics and to a method of preventing redeposition of dirt during the washing of 15 fabrics using the detergent composition.

It is well known that detergent compositions remove dirt from washable fabrics, however, detergent compositions normally have an antiredéposition agent added thereto to prevent 20 dirt that is removed from fabric and is suspended in the wash water from being redeposited on the cleaned fabric prior to removal of the fabric from the wash water.

Perhaps the most well-known antiredéposition 25 agent is sodium carboxymethyl cellulose which has been known to be an effective antiredéposition aid in powdered detergents for many years. In the testing of the efficiency of an antiredéposition agent, at test has been 30 devised to indicate the whiteness retention properties of detergent systems and the test measures the increase or decrease of apparent reflectance when the fabric is washed. In order to obtain control of the test procedure, it 35 is necessary that the same surfactant, same fabric and washing conditions be retained with the only change being the antiredéposition agent added to the synthetic detergent. Numerous antiredéposition aids have been 40 evaluated for use with synthetic detergents, among them being carboxymethyl cellulose, non-ionic water soluble polymers such as polyvinyl alcohol and polyvinyl pyrrolidone. However, to date, none have been found acceptable 45 for use with liquid detergents due to the efficiency and economics required to compete in

the detergent field. Carboxymethyl cellulose has been found to be the most economically feasible for the powdered detergents due to its efficiency, availability and economy. The use of carboxymethyl cellulose has several disadvantages, however, even in powders, among them being its tendency to form a flocculent precipitate in the wash water as well as the difficulty encountered in dissolving carboxymethyl cellulose without the use of a wetting agent such as a glycol. Carboxymethyl cellulose is not useful in liquid detergents due to its propensity to cause phase separation.

Briefly described, this invention provides a detergent composition containing from 0.25 per cent to 5 per cent of a maleic anhydride-conjugated diene copolymer salt and 95—99.75% by weight of a synthetic detergent and also a method of preventing redeposition of soil on fabric being washed utilizing a synthetic detergent composition comprising the step of adding to the synthetic detergent, prior to use, from 0.25 per cent to 5 per cent of a maleic anhydride-conjugated diene copolymer salt. In this specification all percentages are by weight unless otherwise specified.

The preferred conjugated dienes that may be copolymerized with maleic anhydride are butadiene and isoprene. Other conjugated dienes that may be used are 2 - chloro - 1,3 - butadiene; 2,3-dichlorobutadiene; 2,3-dimethylbutadiene; piperylene; 2,4-hexadiene; 2 - methyl - 1,3 - pentadiene; 2 - ethyl - 1,3 - butadiene; 2 - propyl - 1,3 - butadiene; 2 - phenyl - 1,3 - butadiene; 3 - methyl - 1,3 - pentadiene; 2 - ethyl - 1,3 - pentadiene; 2 - methyl - 1,3 - hexadiene and 1 - methoxy - 1,3 - butadiene.

The reaction may be carried out by placing the maleic anhydride in any organic solvent in which the conjugated diene or dienes are soluble and which is inert towards maleic anhydride, i.e., any solvent which does not contain reactive hydrogen atoms such as alcohols, mercaptans or amines. The conjugated diene and catalyst are preferably added over the total

50

55

60

65

70

75

80

85

90

reaction time. Suitable solvents include 5 ketones, esters, ethers, as for example, acetone, methyl ethyl ketone, cyclohexanone, ethyl acetate, butyl acetate, dioxane, tetrahydrofuran, dipropyl ether, dibutyl ether, dimethyl ether of ethylene glycol or dimethyl ether of diethylene glycol. The above polar solvents are generally preferred since they are usually 10 solvents for the copolymer as well as the monomers, and maintain a homogeneous phase throughout the reaction period.

The salt of the polymer is prepared by reacting 15 an organic or inorganic base with the acid or, in some cases, the anhydride form of the polymer. The preferred bases utilized to prepare the salt are alkali metal hydroxides, e.g. sodium or potassium hydroxide, basic alkali metal compounds such as oxides, carbonates and bicarbonates, e.g. sodium oxide, potassium bicarbonate and sodium carbonate, ammonium hydroxide or anhydrous ammonia, and amines, e.g., alkanolamines, hydroxides formed by substituted amines and quaternary 20 substituted ammonium hydroxides. Partial salts (e.g., when 10—100 per cent of a stoichiometric amount of base is added to the acid form of the polymer) are also useful as 25 antiredeposition agents in this invention. The detergent compositions of this invention may 30 also be prepared by adding the acid or anhydride form of the maleic anhydride-diene polymer to a detergent composition that contains basic salts. The antiredeposition agents are thus formed *in situ* by a neutralization 35 reaction.

The specific detergents that may incorporate 40 the antiredeposition agents of this invention may include such compounds as alkyl arylsulfonates, alkyl sulfates and ethoxylated alcohol sulfates. However, the detergents are relatively unimportant and the invention is not limited to any given detergent.

As an example of the preparation of the 45 antiredeposition agent, a specific copolymer, i.e., a maleic anhydride-butadiene copolymer was prepared as follows. 0.153 moles (15 g.) of maleic anhydride was placed in a 100 ml. three-necked reaction vessel equipped with a magnetic stirrer, gas inlet tube, condenser and 50 thermometer along with 13 ml. of peroxide-free dioxane. 0.25 g. of benzoyl peroxide were added to the reaction vessel. After stirring for five minutes, 0.153 moles, 7.7 g. of butadiene were added by distillation through a tube 55 placed beneath the surface. After an induction period of eight minutes, a vigorous exothermic reaction ensued and an increase in viscosity was noted. The maleic anhydride-butadiene copolymer (2 g.) was isolated by 60 precipitation with benzene. The copolymer softened at approximately 140°C. and was soluble in dimethyl formamide and acetone. The product was hydrolyzed and reacted with

a stoichiometric amount of ammonium hydroxide to form the ammonium salt. 65

As previously mentioned, the evaluation of an antiredeposition aid is based, in nearly all cases, on reflectance measurements to determine the amount of soil on a given fabric following a wash cycle or cycles. In demonstrating the usefulness of the antiredeposition aids of this invention, the maleic anhydride-conjugated diene copolymers were compared with carboxymethyl cellulose in a standard built alkylarylsulfonate detergent and with "Tide", (Registered Trade Mark) a commercial heavy-duty anionic detergent. In the examples listed below, the maleic anhydride-butadiene copolymer salt was placed in a detergent and compared with the same detergent containing carboxymethyl cellulose and both of these laboratory prepared detergents were compared to "Tide" as a standard. The fabric was washed in four separate laundering cycles. In the examples, the washing machines were loaded with five standard soiled swatches, five heavily soiled restaurant towels, eighteen 6"×6" clean, white Indian Head fabric swatches and one cup of the respective detergent. Each load was dried between wash cycles in separate dryers. After drying, one of the standard soil swatches was removed from each machine, as well as three of the Indian Head swatches to be used for reflectance measurements following each cycle. The quantity of detergent used as well as the active ingredients of the liquid detergents were added so as to correspond with the "Tide" used on a weight basis. The specific soiling agents utilized in the examples were commercial heavily soiled restaurant towels and United States Testing Co. standard patented soiled cotton cloth. The formulation utilized as well as the reflectance measurements after each wash cycle are set forth in the table hereinbelow. 70

The compositions set forth in columns A, B, and C using the maleic anhydride copolymer were clear and temperature stable compositions that did not form separate phases upon standing. It will be noted that the formulations of A, B, and C below were prepared so as to be high in solids content (50% +), which cannot be accomplished using carboxymethyl cellulose. It will also be noted in Column D that the amide which is used in most commercial formulations of ionic detergents is not necessary in this ionic detergent formulation. 75

In our copending Application No. 15937/69 (Serial No. 1260514) we describe *inter alia* a detergent composition which comprises from 0.1% to 5% by weight of a maleic anhydride-conjugated diene copolymer, the free acid derived therefrom or a water-soluble salt of the acid. 80

65

70

75

80

85

90

95

100

105

110

115

120

125

TABLE 1

	A	B	C	D
Water	270 ml.	270 ml.	270 ml.	270 ml.
Carboxymethyl cellulose 7L	5 g.	—	—	—
Ammonium Salt of Maleic Anhydride-Butadiene-IV 0.25* (10% Solids)	—	5 g.	—	5 g.
Ammonium Salt of Maleic Anhydride-Butadiene-IV 0.58* (20% Solids)	—	—	5 g.	—
Propylene Glycol	10 g.	10 g.	10 g.	10 g.
Tetrapotassium Pyrophosphate	180 g.	180 g.	180 g.	180 g.
SXS Hydrotrope — Sodium Xylene Sulfonate 40 per cent	190 g.	190 g.	190 g.	190 g.
LAS (Sodium Alkybenzene-Sulfonate) 60 per cent	266 g.	266 g.	266 g.	266 g.
Amide (Coconut Diethanolamide)	40 g.	40 g.	40 g.	—
Sodium Silicate	50 g.	50 g.	50 g.	50 g.
Optical Bleach (Sandoz TH-10)	0.3 g.	0.3 g.	0.3 g.	0.3 g.
Physical Appearance After Two Hours	Cloudy and separate phase	Clear and one phase	Clear and one phase	Clear and one phase
Per cent Solids	50.5	50.5	50.5	47.2

The swatches from each wash cycle were submitted for reflectance measurements, which are recorded below.

Indian Head

Washer	Tide	A CMC	B IV.25	C IV.58	D IV.25
Cycle 1	87.94	88.38	88.31	88.49	87.44
2	88.46	89.57	87.90	88.27	88.01
3	88.48	88.70	88.12	87.78	87.29
4	88.57	86.71	87.18	83.47	84.95

Standard Soil — Detergency Rating

Washer	1	A	B	C	D
Cycle 1	30.58	33.65	30.65	33.89	32.91
2	28.65	34.09	32.61	29.97	31.84
3	28.87	28.52	28.73	30.07	32.79
4	29.81	34.71	30.02	32.60	34.51

* Inherent Viscosity of Anhydride — 0.2 g. dl/c measured in dimethyl formamide at 25° C.

WHAT WE CLAIM IS:—

1. A detergent composition comprising from 95 per cent to 99.75 per cent by weight of a synthetic detergent and from .25 per cent to 5 per cent by weight of a maleic anhydride conjugated diene copolymer salt. 25

2. A composition according to claim 1, wherein the conjugated diene is butadiene or isoprene. 30

3. A composition according to claim 1 or 2, wherein the copolymer salt is prepared by reacting the acid form of the copolymer with an alkali metal hydroxide, alkali metal oxide, alkali metal carbonate, alkali metal bicarbonate, ammonia, amine, hydroxide of a substituted amine or a quaternary substituted ammonium hydroxide. 35

4. A composition according to any one of the preceding claims, wherein the detergent composition is a clear homogeneous continuous phase liquid detergent. 35

5. A composition according to any one of

the preceding claims, wherein the copolymer salt is prepared by reacting the acid form of the copolymer with ammonia.

6. A detergent composition according to claim 1 substantially as hereinbefore described.

7. A method of preventing redeposition of dirt on washable fabrics that are being washed as a detergent comprising the steps of adding to the detergent from 0.25 to 5 per cent by weight of a maleic anhydride-conjugated diene copolymer salt and adding the detergent/copolymer salt composition to a washing cycle during the cleaning of the fabric.

8. A method of preventing redeposition on dirt on washable fabrics according to claim 7 substantially as hereinbefore described.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn, London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.